Ultra-Clean Sample Filtration (FGS-029)

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1.0 SCOPE

1.1 This method allows the determination of dissolved trace metals in water and aqueous industrial and municiple effluents. The method can be employed to obtain sediment porewater concentrations, provided the sediment has a sufficiently high water content, and appropriate attention is paid to the redox condition and handling of the samples.

2.0 METHOD SUMMARY

2.1 Unpreserved samples are vacuum filtered in the laboratory through acid cleaned cellulose nitrate membrane filters contained in disposable polystyrene filtration units. The choice of pore size is determined by project specific needs, but in general a 0.45 μ cut off us used in ambient and waste water sampling. In the event that the particulate phase on the filter is to be retained for analysis, the same procedure is applied using a re-usable Teflon or polysulfone filtration unit with replaceable membrane filters.

2.2 For in-field filtration of samples, particularly important for anoxic and ground waters, an acid cleaned pleated filtration cartridge is placed in line with the pump tubing, and the sample filtered directly as it is collected.

3.0 MATERIALS AND EQUIPMENT

3.1 Disposable Nitrocellulose Filtration Units. Disposable polystyrene units of various volumes (100-1000 mL), containing a non-removable 47 mm diameter nitrocellulose membrane filter (Nalge, or equivalent). These units, used primarily for tissue culture sterilization, come in 0.2 μ, 0.45μ, and 0.8 μ pore sizes.

3.2 Individual Nitrocellulose Membrane Filters. 47 mm diameter nitro cellulose filters available in a variety of pore sized from 0.1 μ to 8 μ (Millipore or equivalent).

3.3 Vacuum Filter Holder. Any Teflon, polycarbonate, or polysulfone filter holder designed to hold 47 mm filters, and allow retrieval of both the filtrate and filter. The filter holder should be acid cleaned (FGS-007), and stored in dilute HCl or dried and double bagged until use.

3.4 Disposable Pleated In-Line Cartridge Filter. Filter unit consisting of a polycarbonate or polysulfone shell, containing a large area pleated membrane filter (polycarbonate or nitrocellulose) of specified pore size and surface area (Gelman or equivalent). Larger cartridges are used for larger volumes or in waters with higher suspended solids loading.

3.5 Teflon end-plugs. Depending upon the size of cartridge filter selected, Teflon endplugs must be fabricated which may be attached to the tubing connectors of the unit after cleaning. The plugs, equal to the diameter of the fittings (generally 0.5 inch), and 2 inches long, are acid cleaned according to FGS-007. They are attached to the fittings using bits of dilute acetic acid-cleaned silicone rubber or C-Flex tubing.

3.6 10% (v/v) Hydrochloric Acid. Low-trace metals reagent grade HCl dissolved in 18 meg Ω water.

3.7 Deionized Water. 18 meg Ω DI water, previously tested, and certified low in the trace metals of interest.

3.8 Vacuum Pump. Laboratory vacuum filtration pump, with in-line sub-micron filter between pump and filtration unit, to avoid contamination of sample by pump during on/off cycles.

3.9 Teflon Coated Filter Tongs. Stainless steel filter tongs with Teflon coating. Should be cleaned in dilute HCl before each use, dried in clean air hood, and stored in clean-room when not in use.

3.10 Teflon vials. Ultra-clean (FGS-007) 25.6 mL or 18.2 mL Teflon vials (Savillex), rinsed and dried in the clean air hood. Used to store/digest the 47 mm filters, if particulate metals are to be determined.

3.11 Teflon Bottles. Ultra-clean (FGS-007) 125 mL to 1000 mL Teflon bottles (Nalgene), rinsed and dried in the clean air hood. Used to store/digest the filtrate, until trace metal analysis.

4.0 METHOD

4.1 Procedure using disposable filtration units (perform in cleanroom).

4.1.1 Several hours before filtration is to begin, fill the upper reservoir of the requisite number of filtration units with 10% HCl. Allow the acid to slowly percolate through the filter unit, under gravity (no vacuum), until at least half the volume has passed through.

4.1.2 After two hours of percolation, apply vacuum to pull the remaining acid into the bottom reservoir, shake to wet all inside surfaces, and allow to stand at least 30 minutes. If the filtration unit has greater

reservoir capacity than funnel capacity, pour sufficient DI water through the unit under vacuum to fill the reservoir, shake, and then allow to stand 30 minutes.

4.1.3 Empty acid from bottom reservoir, reassemble unit, and fill upper reservoir with DI water. Use vacuum pump to pull water through to bottom reservoir.

4.1.4 Repeat step 4.1.3.

4.1.5 Filter water sample exactly as for DI water in 4.1.3. Continue to apply vacuum until either (a) enough volume has been collected, or (b) 20 minutes after flow of filtrate comes to a slow drip.

4.1.6 Open filtration unit carefully (wearing cleanroom gloves), and pour filtrate into appropriately sized Teflon bottle. Preserve or digest the sample as appropriate for the desired analysis.

4.1.7 Discard filtration unit.

4.1.8 For every set of filtrations (or for every 10 filtrations, which ever is sooner), a filtration blank should be determined. To determine the filtration blank, fill one Teflon bottle with DI water (before filtration blank), and then filter a similar volume of DI water through a previously cleaned filter unit (after filtration blank). The filtration blank is then the difference between the two results for the trace metal of interest.

4.2 Procedure for sediment pore water.

4.2.1 The procedure for sediment pore water is exactly the same as for water, except that the sediment is homogenized, and then poured into the funnel of the filtration unit. The sediment must be agitated to allow a seal to form between the sediment and the filter. Failure to do so will result in channeling of air, and no successful pore water extraction.

4.2.2 Sediment clogs the filtration unit very rapidly. Usually the sample is filtered for 20-30 minutes, resulting in the collection of 10-30 mL of pore water.

4.2.4 Oxic sediments (containing an air space in the container) may be filtered in the ordinary lab. Anoxic sediments (sealed in an airtight container in the field) must be filtered under N_2 in a glove box.

4.3 Procedure for the use of discrete filters (of filtrate and particulates)

4.3.1 The procedure followed is as for disposable units, except that a re-usable unit, loaded with a discrete filter is used.

4.3.2 Filters must always be handled with clean filter tongs. Use care to avoid puncturing the filter during handling.

4.3.3 If the particulate matter on the filter is to be analyzed as well as the filtrate, after the water over the filter is sucked dry, the filter is carefully folded in half with the tongs, and placed into a Teflon vial until digestion.

4.3.4 Reusable filtration unit should be thoroughly rinsed with DI water before each

re-assembly and re-use. Then follow cleaning steps for filter as outlined in 4.1.

4.4 Procedure for in-line field filtration.

4.4.1 Filtration cartridges are cleaned by submerging into a large beaker or vat filled with 10% HCl. The units must be coaxed to fill completely with acid, with no air bubbles. Filter units are soaked in acid for a minimum of 2 hours.

4.4.2 After acid cleaning, rinse exterior of unit with DI water, and then attach cartridge inlet to DI water tap, and pass DI water through for a minimum of 10 cartridge volumes (5 minutes at 0.5 litres/min, for a typical 250 mL cartridge volume).

4.4.3 Allow all liquid water to drain out of cartridge by gravity, and place units into clean air hood to dry off exterior. Then plug end with Teflon plugs, and double bag until transport into the field.

4.4.4 In the field, use the "clean hands-dirty hands" technique (FGS-008) to place the cartridge in the pump line, and obtain a filtered sample. Be sure to discharge at least 1 filter unit volume (preferably 3 volumes) before collecting sample.

4.4.5 Discard filtration unit after each sample.

4.4.6 Blanks are obtained (either before or after the field mission) by filtration of DI water directly from the tap, discarding 3 cartridge volumes before collection of the blank sample. Obtain an unfiltered DI water

sample as the before filtration blank at the same time. Al least one set of filtration blanks per set, or per 10 samples, which ever is sooner should be collected.

5.0 QUALITY ASSURANCE AND WARNINGS

5.1 Method blanks, encompassing a before filtration and after filtration blank of DI water should be collected as described in section 4. Blank pairs should be collected once per sample set or per 10 samples, which ever is sooner.

5.2 The cleanliness of the method has not thoroughly been checked for metals other than mercury, so additional blanks should be conducted initially for these metals. The typical blank contribution for mercury has been found to be 0.0 ± 0.1 ng/L for in-lab filtration, and 0.5 ± 0.5 ng/L for field filtration.

5.3 Do not filter samples to be analyzed for volatile Hg species, as these will be lost under vacuum.

5.4 Limited studies have indicated that the dissolved/particulate fraction (Hg) of oxic lake, river, ocean, and rain waters is constant over a period of days to weeks, when the raw samples are stored cool and dark. FGS protocol requires filtration of raw samples within 48 hours of collection. Storage of unpreserved samples always runs the risk of wall losses. These should be investigated on a project specific basis.

5.5 Anoxic and low oxic waters, especially ground waters, must be field filtered in-line. Failure to do so may result in dramatic wall losses on precipitated iron and manganese oxides.

5.6 In-line field filtration is the only EPA accepted methodology.

5.7 Filtration of water containing free cells at pressure differentials of > 3 psi may result in cell rupture, and loss of cytoplasm into the dissolved phase.

5.8 Filtration of acidified samples is meaningless. In clear waters with high sediment loads, the dissolved fraction will be over estimated due to desorption from particles In brown waters, the dissolved fraction will be under estimated due to humic coagulation.

5.9 Wall loss related errors are minimized by collecting two samples for lab filtration studies. One of the samples is digested in the bottle unfiltered, and the other sample is filtered, and then placed back into the original bottle, after rinsing with DI water to remove clinging particulates. Any dissolved Hg lost to the walls is thus re-incorporated into the dissolved sample upon acidification/digestion.

6.0 REFERENCES

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